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REMOTE SENSING

Environmental Effects of Surface Films

Final Report

12 December 1989

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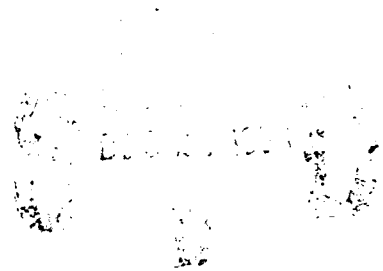


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1.0 BACKGROUND

This report describes a portion of a program involving both experimental and theoretical studies of the influences of natural biogenic sea surface films on air-sea interfacial parameters. In addition, the role of physical processes in the marine environment on the film's state, lifetime, and transport is being investigated. Initial objectives included the determination of the effects of (1) currents on film formation and intensity, (2) surface films on waves, (3) surface films on wave/current interactions, and (4) surface films on near-surface turbulence. During the planning phase of the program these objectives were refined to emphasize the following specific subject areas:

- (1) Film transport and modulation by currents
- (2) Film involvement in wave-induced Langmuir instability
- (3) Film effects on sensible temperature including the determination of T as a function of the surface elastic modulus, and the time scales involved in the development of the temperature effects

2.0 REVIEW OF PROGRAM ACTIVITIES

1. ORINCON Principal Investigator W. D. Garrett, has performed several functions within this program, including ongoing consultation with the program manager. In the initial stages of the program, a three-day workshop was organized to review the knowledge base and develop a tentative multiyear research and assessment program. Prior to the workshop, issues, objectives, and tentative approaches were developed to formulate a base for the experimental/theoretical program. Considerations included model development, tank studies, and coordinated multidisciplinary field experiments. As technical advisor to the program manager, advice was provided on workshop and program participants. The workshop report was refined through numerous iterations and consultation was provided on the prioritization of the proposed tasks.

2. A document has been prepared which addresses surface film deployment and measurement strategies and surface film selection criteria. This report includes specific recommendations on choices of (1) a physical model surface film; (2) a chemical model film and (3) techniques for the collection of natural organic sea-surface, film-forming material for use in laboratory tank studies.

3. A 07 DEC 88 meeting has held with program participants at TRW, Los Angeles, to (1) prioritize experiments, (2) discuss measurement methodologies, and (3) review the chemical (organic surface film) aspects of the experimental program. These considerations were subsequently discussed with the program manager on 21 DEC 88, at which time the sequence and nature of the experimental/modeling efforts were reviewed in detail. Experiments to be initiated in FY-89 included (1) film transport and modulation by currents, (2) wave-induced Langmuir instability, and (3) film effects on effective temperature. A presentation was made on surface film issues which was based upon research and analysis performed within the last several months. Surface film selection criteria were developed, taking into account a number of factors including viscoelastic parameters, chemical structures, and the nature of the planned laboratory experiments. Three organic films were identified as physical models of natural films, and natural seawater was found to an appropriate film-forming medium for one of the principal experiments.

4. The possible use of an at-sea bubble generator for the concentration of natural surface-active organic material was evaluated within this reporting period. However, the quantity of active organic material collected by this device was not sufficiently large for use in the planned laboratory experiments. The three acceptable model-film chemicals will be acquired and delivered to the laboratory facility as soon as possible. Film development strategies and measurement methodologies have been suggested for the determination of film motion, surface tension, and surface elasticity.

5. Three appropriate materials were selected, acquired, and delivered to TRW, Redondo Beach, CA, where tank experimentation is being performed. A surface marking substance was also proposed. Recommendations for experimental strategies were developed which included types of surface films to be used and their methods of deployment and manipulation on experimental water surfaces. The specific film-forming material or natural seawater film was related to the nature of the oceanic process being studied and the characteristics of the experimental facilities. During the period 21-23 June 89, ORINCON Principal Investigator W. D. Garrett, worked at the TRW research tank facility to integrate the surface films into the various experimental schemes. Work included, (1) the production of spreading solutions capable of yielding appropriately low surface concentration of surfactants, (2) demonstrating film deployment techniques, and (3) participating in calibrations of a surface

tension/elasticity sensor to be used in film effects studies. Film pressure vs. area curves were prepared from a quadratic equation based on experimental data. These curves were used to determine the quantity of material required to produce specific surface concentrations and film conditions.

6. On 2 July 89, these activities were reviewed for the program manager and for a review group of scientific experts in San Diego, CA. During the period June to September 89, consultation was provided to the TRW research team studying (1) film transport and modulation by currents, and (2) wave-induced Langmuir instability. Plans were discussed and formulated for out-year laboratory tank studies involving organic surface films.

3.0 SELECTION CRITERIA

The primary criterion for the selection of organic surface films for wind-wave tank research in this program is that the experimental films resemble natural organic slicks as closely as possible. Ideally, the chosen film should match those in the real world in both chemical constitution, rheological properties, and most importantly, the film effects on air-sea interfacial parameters and processes. In experiments involving tanks, it might be feasible to import freshly-collected sea-water to achieve the most realistic surface film conditions. Seawater will be recommended for certain experiments in this program, and the special water surface manipulations required will be addressed in a subsequent section.

Present technology in marine microlayer sampling and characterization does not allow for either the collection or synthesis of a truly natural film for laboratory experimentation. However, three model film approaches are recommended in order to approximate a natural sea-surface film as closely as possible. These include (1) a model film based on visco-elastic properties, (2) a model film formulated to duplicate the chemical constitution of natural organic slicks, and (3) natural film-forming substances concentrated and collected by a bubble-scavenging system which can be operated at sea.

4.0 CLASSES OF EXPERIMENTAL SURFACE FILMS

4.1 The Physical-Model Film

Film pressure vs. area isotherms have been measured on natural films collected by surface-microlayer samplers (Barger, Daniel, and Garrett, 1974). Barger (1985) has compared numerous film pressure area plots for films on natural waters with those of chemically known, surface-active agents, in order to derive knowledge of the hydrophil-lipophil (HLB) balance of the natural films. Several commercially available surface active compounds formed films that exhibited strong similarities in their visco-elastic properties with films formed on natural seawater. Of these PEG 200 monolaurate is readily available and is recommended for study. Obviously this physical model film is a synthetically produced material and does not resemble the natural condition in a chemical sense. However, this physical-model film mimics visco-elasticity and the HLB of natural films as well as their partial solubility characteristics. Since these physical considerations determine the influence of the film on the physics of the air-water interface, PEG 200 monolaurate should be included in film-effects research. In addition, oleyl alcohol and triolein are recommended as being similar but not identified to the surface physics of natural films. There is large quantity of scientific literature devoted to at-sea studies of the effects of monomolecular films of oleyl alcohol on sea surface physics and remotely sensed imagery.

4.2 The Chemical Model Film

Sea surface microlayer collections have been chemically analyzed by several investigators. The composition of natural films is spatially and temporally variable and depends upon numerous physical and biological conditions in the marine environment. In addition, the chemical constitution is extremely complex, representing the many classes of materials produced biogenically in the sea. Williams et al. (1986) has attempted to measure the principal chemical classes present in microlayer collections (proteins, lipids, carbohydrates, etc.). Even in this comprehensive study, approximately 60% of the organic film-forming material remained uncharacterized.

On the basis of the research of Williams et al. (1986), the following formulation approximates the chemical constitution of natural film-forming material.

- Protein: heptone from soybeans, C/N approx. 6
- Carbohydrate: alginic acid, MW-240,000 (polymannuronic acid)
- Lipid: triolein, MW=885.4

Mix peptone (25% as carbon), alginic acid (50% as carbon), and triolein (25% as carbon). It should be restated that these three components account for only 40% of the total carbon in a natural film. The remaining 60% is almost completely unknown chemically.

The visco-elastic properties of such a mixture have not been determined. Consequently, it is not clear whether this chemical-model film would be of value in studies of film effects on air-sea interfacial properties. On the other hand, this film would have more realistic solubility characteristics than the physical-model film. That is, the more soluble constituents would be excluded from the water surface during straining and compressional events which stress the film. Should the chemical-model film be formulated for use in tank research, its rheological properties must be determined under controlled conditions in a hydrophil balance for comparison with those of natural sea surface material. Because of the unlikely possibility of duplicating the physics of natural films with a chemical model film mixture, this approach is not recommended.

4.3 Bubble-Collected Natural Film-Forming Material

A cylindrical device has been developed and patented (Van Ry, 1987) which generates surfactant-scavenging bubbles in the sea. The resulting foam-water-particle mixture is collected by overflow at the top of the bubble-scavenged water column. The system, available from MAC Industries Inc., Annapolis, MD, has been designed to concentrate the resulting foam and reduce the collected quantity of bulk water. This "slick" sampler/generator will be evaluated as a possible tool to acquire natural film-forming organic material from the sea. If it is feasible to collect sufficient material for tank studies, the resulting material would produce films that are quite realistic, and embody the parameters of both the chemical and physical-model slicks. Furthermore, naturally derived films may provide the only means of adequately studying the problem of surface scare persistence.

It is recognized that this device exaggerates one of the mechanisms by which biogenic slicks are formed. The vigorous bubbling may also lyse marine organisms in a less than natural manner. Organic containing particles and some chemical classes might be collected with concentrations exaggerated over those associated with a more naturally generated surface film.

However, in spite of these shortcomings, this collection device may produce the most realistic oceanic film possible for tank studies. An evaluation of this device in May 1988, included an assessment of its ability to collect and concentrate film-forming organics in the foam-particle mixture produced by the floating bubble collector. The collected bubble-scavenged organics were spread into a hydrophil balance for film pressure vs. area characterizations of the resulting surface films. The area of the film formed from a specific volume of bubble-collected material was determined so that collection quantities required for experimental tank coverage could be calculated.

It was determined that one ml of collected foam liquid produced 1.07 square centimeter of film when spread into a water surface at film pressure of 5 mN per meter. Thus, 9.3 liter of foam concentrate would be required to cover one square meter of water surface with a monomolecular film. Since the experimental tanks used in this research have 10-20 square meters of surface areas, exorbitant quantities of foam mixture would have to be collected and transported. Furthermore, spreading of such large quantities of foam mixture onto the experimental tank surface would be extremely slow and tedious with no guarantee that a successful film could be maintained for the time periods required for an experiment.

4.4 Films From Natural SeaWater

Natural seawater is difficult to collect, transport, and store. However, it represents a source of realistic films, and may be appropriate for certain experiments in low-volume tanks. When it is possible to use freshly collected seawater, the following procedures should be followed to handle the films formed from the natural organic surface-active substances present. Seawater is added to the tank and allowed to come to an equilibrium state with regard to turbulence, temperature, entrained air bubbles, etc. During this period of time, an organic film will form at the surface. The surface pressure of this film (a function of the

surface concentration of film-forming molecules) will be determined by the organic richness of the seawater and various transport factors. This film can be manipulated for experimentation by the techniques identified in the ensuing section.

A more controlled experiment would involve cleaning the surface of the film formed during the seawater equilibration, then allowing new film to form gradually by adsorption of film-forming polar molecules. This is a relatively slow process. The transport of polar molecules will be diffusion controlled if there are no other vertical transport processes (bubbles or thermal upwelling) in the experimental tank. The surface properties of the films and the air-water interfacial properties affected by them can be determined as the film develops by adsorption from the bulk seawater substrate.

5.0 SURFACE FILM DEPLOYMENT

Spreading of monomolecular organic films over the surface of a laboratory tank can be readily accomplished even under wind-wave conditions if the film-forming material has the following properties. The surface-active substance should be fluid, spontaneously spreading and autophobic. Autophobicity is a property of relatively pure, surface-active fluids, where the excess film-forming material does not spread over its own monomolecular layer. Instead, the excess remains in spreading equilibrium with the monolayer as an unspread liquid lens at the monolayer collapse pressure. The unspread excess acts as a reservoir to replace monolayer lost to film-dispersive processes, such as evaporation, dissolution, wind-wave dynamics, etc. Continuous controlled addition of such a material results in a uniform monolayer over a wind-driven tank water surface with the film at its maximum (collapse) pressure.

Film-forming materials which are autophobic include oleyl alcohol (cis isomer of 9-octadecen-1-ol), glycerol trioleate, and PEG (200) monolaurate. The latter compound is the physical-model agent described in the film-selection section. Oleyl alcohol and glycerol trioleate have been used widely in both tank and field research to demonstrate the physical effects of pure monofilms on air-sea interfacial processes and the resulting modulations of remotely sensed signals. Fluid film-forming chemicals can be dispensed at low, controlled

rates, with a syringe pump onto the upwind end of a wind-wave tank. Dispensing rates for wind-driven experiments can be calculated from the surface concentration required to form a monomolecular layer (1-2 mg/m²) and the wind-driven surface flow (approximately 3.5% of the wind velocity).

An exact value of the surface concentration for a pure material can be calculated from:

$$\text{mg/m}^2 = \frac{\text{MW}(\text{mg/moles}) \times 10^{20} (\text{\AA}^2/\text{m}^2)}{(\text{\AA}^2/\text{molecule}) \times 6.023 \times 10^{23} (\text{molecules/mole})}$$

where the molecular area in square Angstroms (Å²) per molecule corresponds to a point of interest on the surface tension vs. area-per-molecule isotherm.

The rate of dispensing the film forming material (mg/sec) into a fully compacted monolayer is the calculated surface concentration (at equilibrium collapse pressure) in mg/m² times the wind-driven surface flow (m/sec) times the width of the tank in meters. This value is the rate required to account for surface renewal caused by the wind-surface coupling.

When no wind is involved or when an experiment requires the use of less than fully compacted monofilm, equation (1) is used to calculate surface concentration. It is also possible to perform experiments at surface concentrations below that where water surface parameters are effected, in order to study strain-generated films and their surface effects.

If it is possible to collect sufficient film-forming material for tank studies with the in situ bubble generator (section 1.3), a different form of spreading onto the tank-water surface is required. The natural organic surfactants will be part of a bubble-particle-water mixture. This fluid should be allowed to flow at calculated rates down an inclined plane onto the water surface. This procedure allows the polar organic surfactants to contact and spread across the water surface in the experimental tank. The quantity of the mixture and its rate of dispensing will depend upon the contained concentration of film-active material as determined by hydrophil balance studies.

In addition to film-deployment techniques, film manipulation and removal procedures are required. A clean water surface is essential prior to the addition of a known surface film. The simplest cleaning procedure uses wind to drive the largely water-insoluble film to the down-wind end of the tank. Removal by overflow is most effective when it is possible to raise the tank water to the required elevation. Otherwise, vacuum skimming in conjunction with wind is effective in film removal. Floating power (clean talc or PTFE powder) can be added to the residual film to indicate the progress of the removal process. Films may be manipulated on the water surface by movable hydrophobic surface barriers. These may be solid bars or floating waxed cords. The type of surface barrier used depends upon the tank design and the nature of the experiment.

6.0 SURFACE PROPERTY MEASUREMENTS

Measurement techniques for tank water surface properties vary from long-used existing methods to sophisticated systems under development for the Office of Naval Research (ONR) research initiative on marine microlayer processes. The latter suite of measurement systems may someday allow for the continuous in situ measurement of capillary wave attenuation, surface tension, and visco-elastic properties of surface films. At the present time, the accuracy and efficiency of the devices has not been proved.

Existing methods for surface tension measurement are outlined in the *Program Workshop Report*, Systems Planning and Analysis Inc., Feb. 1987. For calm water tank experiments, the Wilhelmy Plate method can provide continuous surface tension measurement at a specific point in the tank. A platinum plate suspended in the surface is attached to a calibrated strain gage or torsion wire. For a less stable, wavy surface, the calibrated spreading oil method (Garrett and Duce, 1980) provides a mobile, but not continuous method of surface tension determination. When used in small quantities, the oils added to the water surface should not modify the experimental results. These oils are not water soluble and will be removed during surface cleaning procedures between experiments.

7.0 CONCLUSIONS

1. In general the physical-model film approach will be emphasized in these studies using PEG (200) monolaurate and oleyl alcohol as the primary film-forming substances. Chemical - model films are not realistic in that they do not duplicate the surface physics of natural organic sea surface films (see figure 5 for experimental surface film options).
2. Thermal infrared studies of film effects on surface temperature and heat flux will be conducted in a relatively small tank. It is recommended that natural, freshly collected seawater, be used in these experiments to provide a realistic surface film condition.
3. Insufficient organic film-forming material is collected by a bubble-scavenging system studied in this project. It is recommended that physical-model films or natural seawater be used in tank experiments (see figures 6 and 7).
4. Whenever possible, noninvasive methods will be used to measure surface tension and the modulus of surface elasticity. If it is not possible to develop and utilize such noninvasive techniques, it may be possible to use low-impact measurements of surface tension, such as the Wilhelmy plate or calibrated spreading oils. In addition, the surface film parameters can be calculated from film-pressure vs. area plots and the quantity of film-forming material added to the tank surface (equation 1 and figures 1-4).

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PEG (200) MONOLAURATE

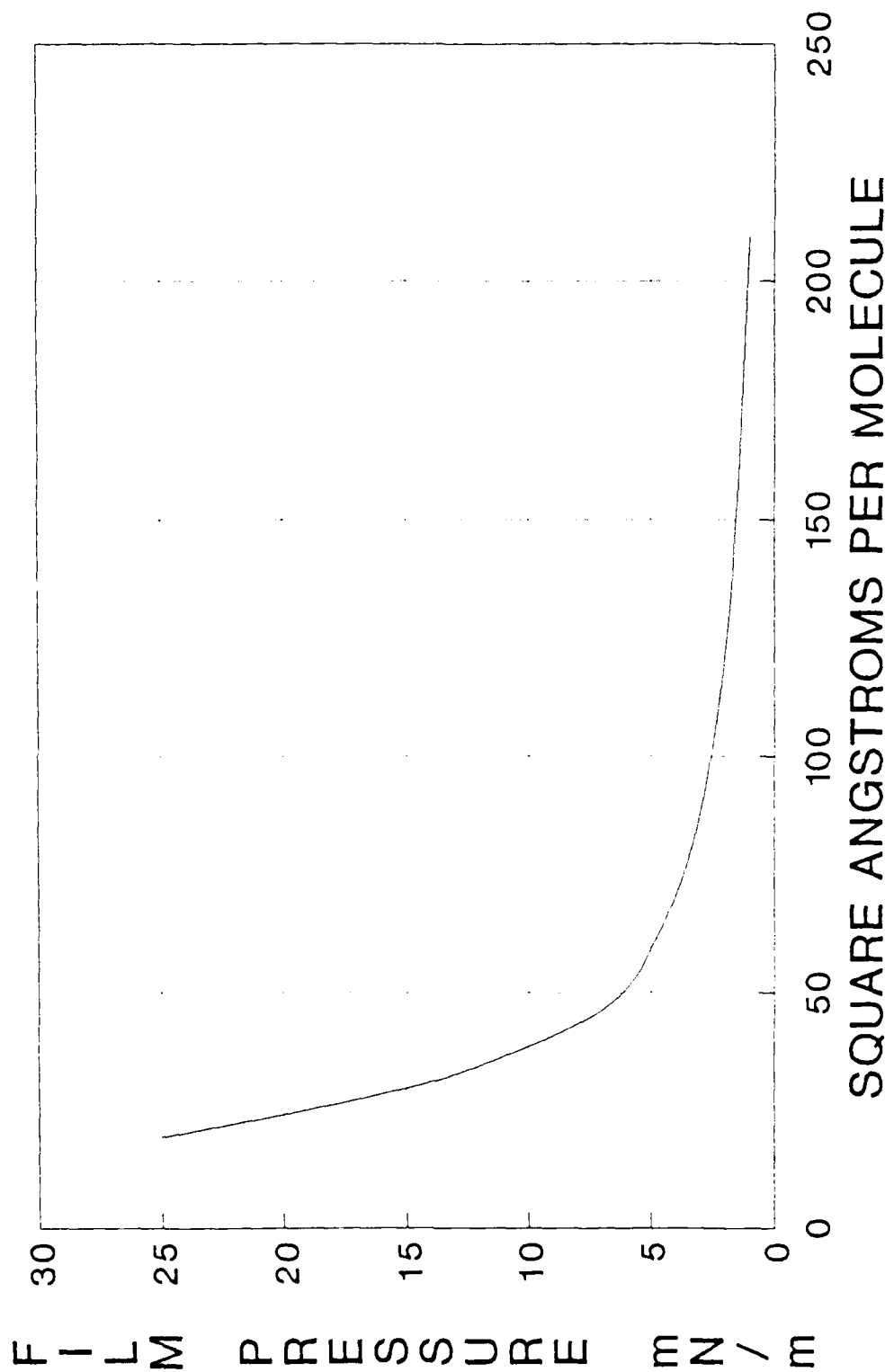


Figure 1. Film pressure vs. area isotherm of PEG (200) monolaurate at 25°C. PEG (200) represents polyethylene glycol groups in the molecule with an average molecular weight of 200.

Plot based on $A = 185/F + 25.1 - 0.52F$

Molecular weight = 3.993×10^5 mg/mole

Specific gravity = 0.984 @ 25 degrees C

OLEYL ALCOHOL

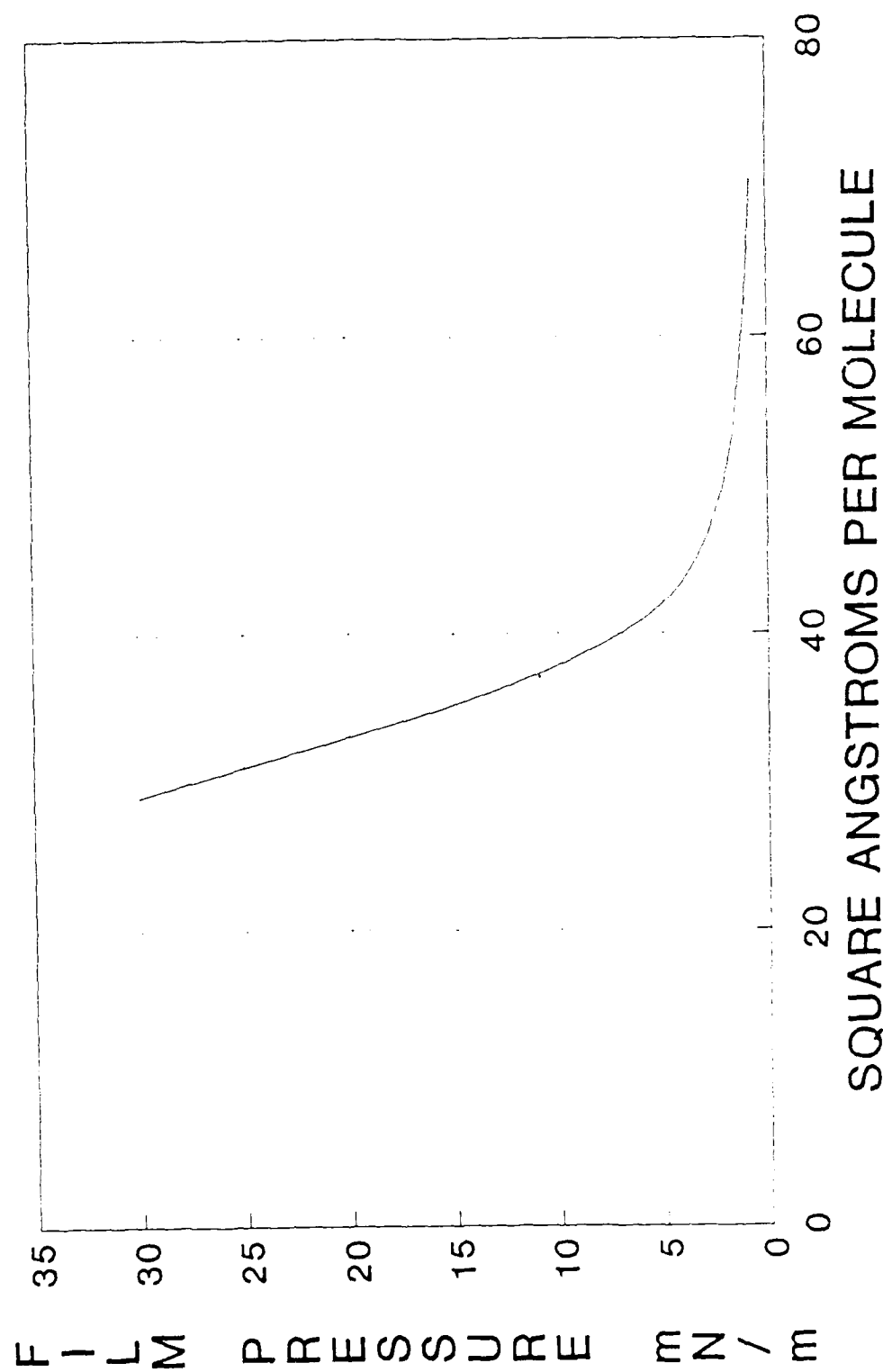


Figure 2. Film pressure vs. area isotherm of oleyl alcohol (cis isomer of 9-octadecen-1-ol) at 25 degrees C.

Plot based on $A = 23.9/T + 38.9 - 0.35F$
Molecular weight = 2.685×10^5 mg/mole
Specific gravity = 0.85 @ 25 degrees C

GLYCERYL TRIOLEATE

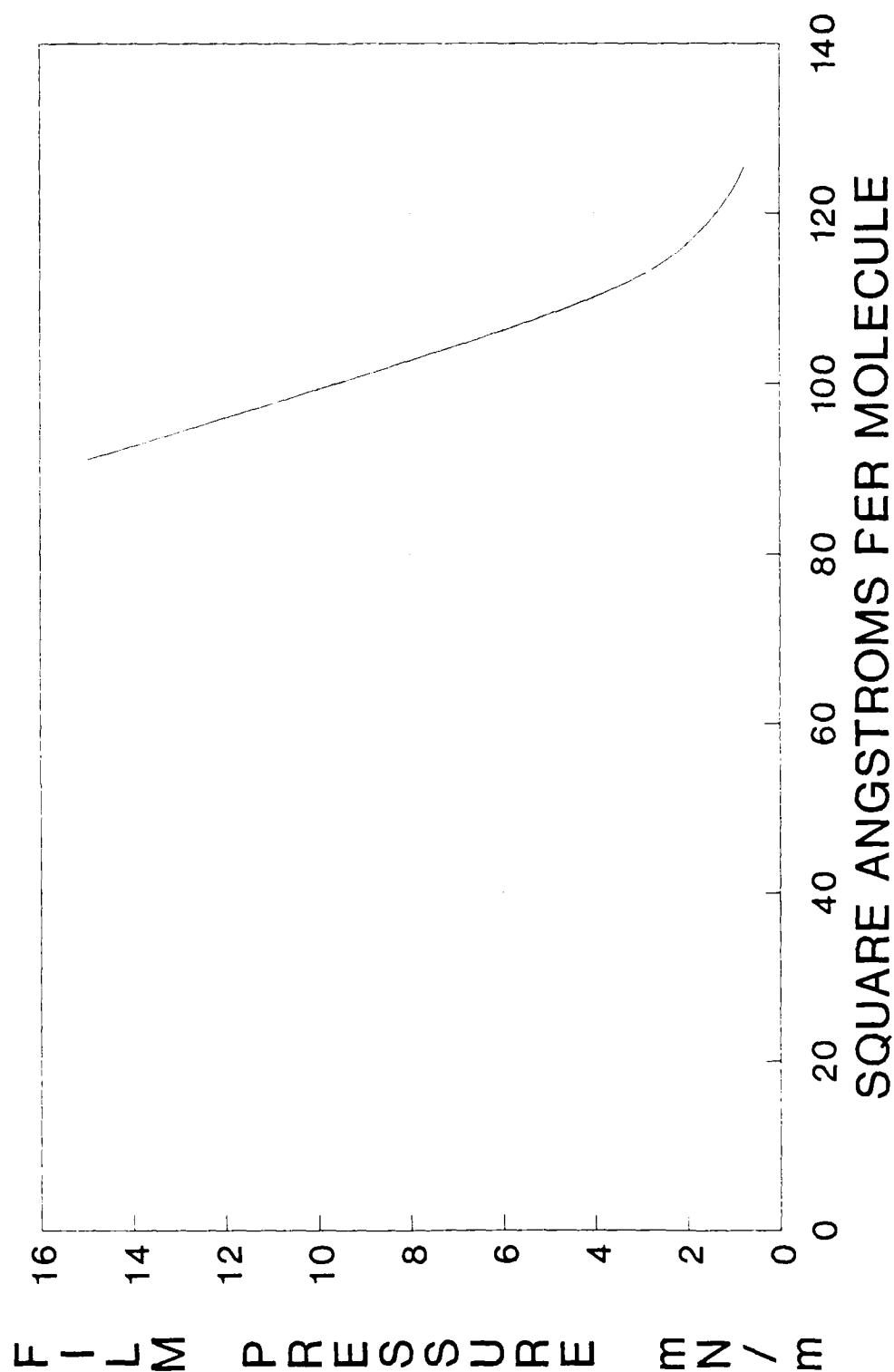


Figure 3. Film pressure vs. area isotherm of glycerol trioleate (triolein) at 25 degrees C.

Plot based on $A = 9.61/F + 114 - 1.57F$

Molecular weight = 8.855×10^5 mg/mole

Specific gravity = 0.916 @ 25 degrees C

PRESSURE VS. AREA ISOTHERM

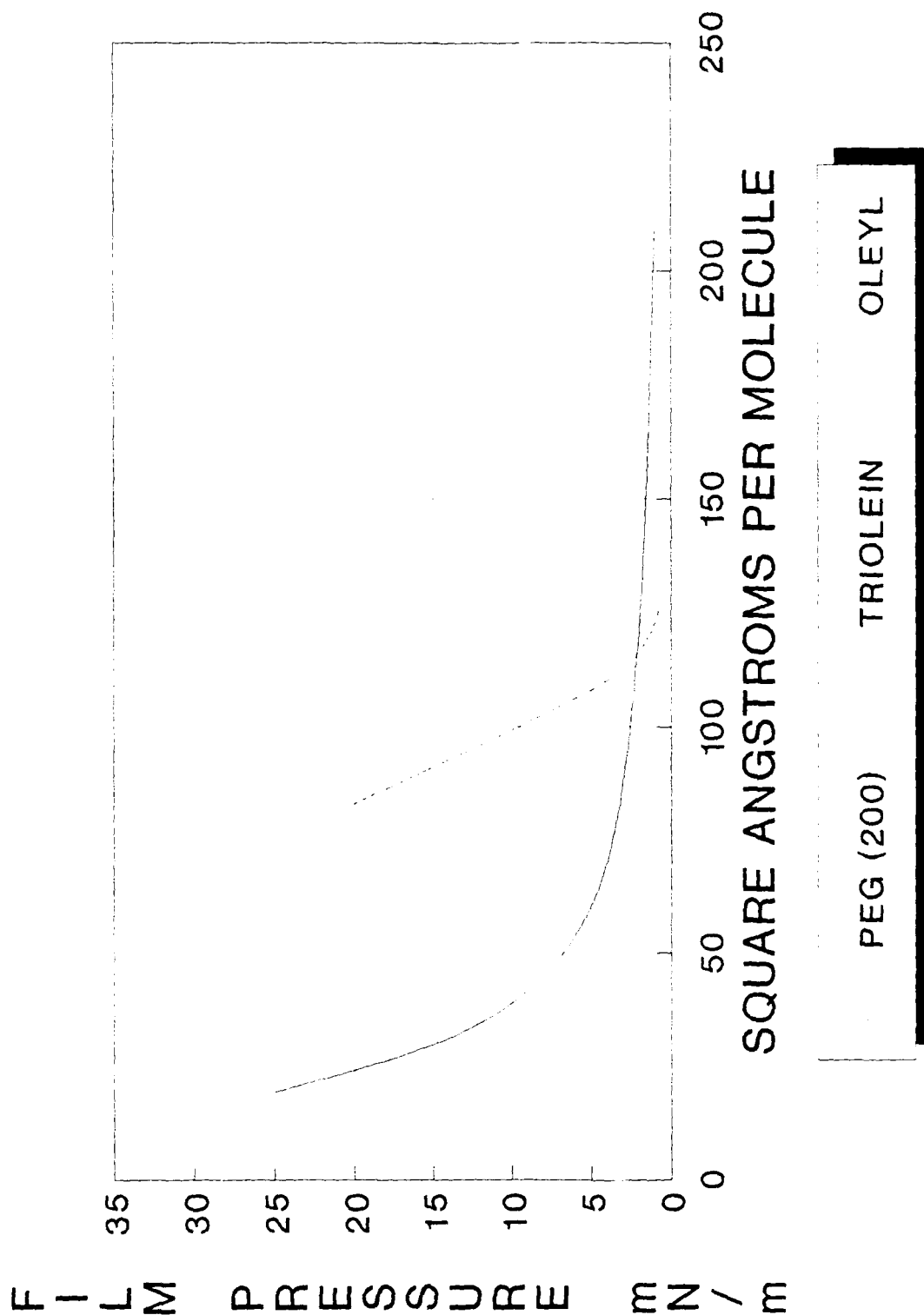


Figure 4. Composite film pressure vs. area isotherms (25°C) for the film-forming chemicals graphed separately in Figs. 1-3.

EXPERIMENT-FILM TYPE

- SURFACE DRIFT/SPREADING

MODEL FILM

- CURRENT TRANSPORT

MODEL FILM

- IR

- ΔT VS. FILM PRESSURE

- EFFECT TIME SCALE

MODEL FILM

SEAWATER

- WIND-WAVE

MODEL FILM

Figure 6. Types of surface films recommended for various proposed tank experiments. Model film refers to the physical-model, film-forming substances plotted in Figs. 1-4 and named in Fig. 3.

SURFACE FILM SELECTION

- **CHEMICAL MODEL**
- **PHYSICAL MODEL**
- **NATURAL**
 - **AIR BUBBLE COLLECTOR**
 - **SEAWATER**

Figure 5. Types of surface films considered in this project for use in experimental tank research on film-environment interactions.

MODEL FILMS-PHYSICAL

- POLYETHYLENE GLYCOL (200) MONOLAURATE
- GLYCERYL TRIOLEATE
- OLEYL ALCOHOL
9-OCTADECEN-1-OL (CIS)

Figure 7. Physical-model films recommended for use in tank experiments on surface film-environmental interactions.